

## **Adsorption of actinide ions from natural waters on specific adsorbents especially designed.**

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The environmental dispersion of the actinides in the hydrosphere, due to many factors and mainly to nuclear power production, represents a very important and interesting radioecological investigation field[1].

Because of the extremely low levels of the actinide ions, the analysis requires a previous concentration step. It seemed worthwhile to the authors to investigate the preparation of specific adsorbents, that are able to isolate and concentrate actinides for analytical purposes, or alternatively for decontamination of polluted ecosystems.

The 8-hydroxyquinoline family and the benzilic (diphenylglycolic) acid have a complexing ability towards the actinides in different oxidation states[2]. Taking advantage of this ability, the salts of benzilic acid with the 8-hydroxyquinoline and with 2-methyl, 8-hydroxyquinoline were prepared and tested. The compounds, owing to the presence of the benzene rings, are easily incorporated into active charcoal to obtain adsorbents with a high specific surface. The method of fixing the adsorbents into charcoal was previously tested [3].

The high affinity of the adsorbent towards the actinide ions represents the necessary condition in order to use small amounts of adsorbent with respect to the large sample volumes involved. Thus a large concentration factor may be reached giving high overall yields and the sensibility of the analysis is enhanced.

For decontamination purposes, besides benzilic acid some phosphates were set because of their great ability to give insoluble salts with many ions in different conditions, and also in the pH range of natural waters. Once saturated, the adsorbents can be removed from the work position, and ignited in order to obtain a product of small size and high insolubility. The adsorbed ions are strongly retained also by the ashes, so the wastes can be successively safely stored.

### ***Experimental Section***

-All chemicals used were reagent grade. Charcoal activated powder (Aldrich and Carlo Erba Analytical, Milano) were used as support of the exchangers.

The adsorption behaviour of uranium, thorium, barium, and europium were studied in batch. Europium was chosen to represent the actinides in the +3 oxidation state, and in some cases barium was chosen to represent radium and strontium. By this way all the actinides in different oxidation state are represented.

In some cases uranium was traced with  $^{239}\text{Np}$ , by irradiation of a few mg of uranyl nitrate in the Triga MarkII 2 Reactor at the University of Pavia at a flux  $2 \times 10^{12}$  neutron  $\text{cm}^{-2} \text{sec}^{-1}$ . After irradiation uranium was treated with conc. nitric acid to assure the formation of the oxycations  $\text{UO}_2^{2+}$  and  $\text{NpO}_2^{2+}$ . In each experiment 1000 Bq of  $^{133}\text{Ba}$

and 1000Bq of  $^{152}\text{Eu}$  were employed after delivery from the carrier free stock solutions, both from Amersham International Ltd (UK).

Uranium and thorium were analysed by Atomic Emission measurements, performed with a Perkin-Elmer ICP - 400

Gamma ray spectra were recorded and analysed with an Ortec Ge(Li) coaxial detector, . 25 % relative efficiency, connected to a computer assisted multichannel analyser.

FT-IR spectra were obtained with a Jasco mod. 5000 apparatus. The spectra were recorded in the range  $4000 - 1000 \text{ cm}^{-1}$  in KBr pellets.

#### *Preparation of the adsorbers.*

--- The 8-hydroxyquinoline and 2-methyl. 8-hydroxyquinoline (to prepare the adsorber **B** and **R** respectively) are mixed with an equivalent amount of the benzoic acid under stirring by gently warming; then activated charcoal is added and, after cooling, the suspended matter is filtered and washed with water, and finally dried. Usually 100 g of base are used for each g of charcoal.

---The same procedure is applied to obtain the benzoic acid incorporated into charcoal starting from benzoic acid, and d-glucosamine. The d—glucosamine was set by considering the complexing ability of glucose derivatives towards uranyl ion: it is not salted by the acid, but is partially incorporated into charcoal (adsorber **G**).

-The content of B, R, and G onto charcoal was measured by treating the adsorbers with NaOH 0.1M, and then filtering off the charcoal. The base and the acid were released in the solution and the back potentiometric titration with hydrochloric acid allowed for the evaluation of the NaOH equivalent excess and the base contribute.

The 8-hydroxyquinolines are present in equimolar ratio with respect to the benzoic acid. The salts incorporated are about 20% of the total adsorber. Only benzoic acid is completely adsorbed in the G case, whereas a smaller amount of d-glucoseamine is present(molar ratio 1:3).

The peaks at  $1593 \text{ cm}^{-1}$  and  $1387 \text{ cm}^{-1}$  (C-O stretching symmetric and antisymmetric), shown by F.T.I.R spectra, indicate that the adsorbers B and R are formed by the salt of the benzoic anion. On the contrary the peak at  $1718 \text{ cm}^{-1}$  confirmed the presence of the free acid in the G case, while the presence of free d-glucosamine is confirmed by the peak at  $2937 \text{ cm}^{-1}$  (N-H). The peak at  $3367 \text{ cm}^{-1}$ , characteristic of the O-H of alcohols, can be clearly observed: it is changed after the adsorption of uranium and thorium.

---Starting from  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in equimolar ratio the adsorber **MG** (magnesium ammonium phosphate) was precipitated and incorporated into charcoal. Likewise starting from  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  in equimolar ratio the adsorber **AL** (aluminium phosphate) adsorbed onto charcoal was prepared

-The analyses of aluminium, magnesium, and phosphorous were carried out with the I.C.P. method after ignition of samples in the presence of sodium peroxide and subsequent dissolution. The analyses gave a ratio 1/1 between magnesium and phosphorous and between aluminium and phosphorous. Usually the adsorbers contain a 11-12% of salt, but the load may be increased when necessary.

*Kd measurements.* About 100 mg of the adsorbers were equilibrated with 10 mL of solution at variable pH. Ionic strength was adjusted to 0.1 by adding, if necessary  $\text{KNO}_3$ , and the pH was adjusted to the desired value with NaOH, acetic acid, Tris or ammonia. Shaking was done for two hours, while maintaining the room temperature.

The initial concentration of radionuclides was  $2 \times 10^{-7}$  mmole / mL. Eu was traced with  $^{152}\text{Eu}$ , and barium with  $^{133}\text{Ba}$ , in order to apply the gamma spectrometry. Comparison between concentration, or activity, before and after adsorption allowed to calculate the distribution coefficients  $K_d$  from the following relationship:

$$K_d = \frac{\text{mmoles (or cpm) of the element adsorbed per g of Adsorber at equilibrium}}{\text{mmoles (or cpm) of the element per mL of the solution at equilibrium}}$$

### Results and Discussion

No detailed adsorption kinetics experiments were done, but the adsorption was checked to reach the maximum after 30 minutes in all cases.

The pH range in which the  $K_d$  values of thorium, uranium, europium and barium are higher than  $10^4$  is reported in Table 1 for each adsorber. In this range the adsorption of the ions under experimental conditions becomes higher than 90%.

Table1. The pH adsorption range for actinides ions on the prepared adsorbers

Adsorber	pH range			
	Thorium	Uranium	Europium (ACIII)	Barium (Radium)
B	> 3.0	6.5 – 9.0	> 4.5	-----
R	> 3.0	> 8.0	> 6.0	-----
G	4.0 –10.0	7.5 –8.0	> 7.0	-----
AL	> 5.5	> 5.5	> 7.0	> 10.0
MG	> 5.5	> 5.5	> 7.0	> 8.0

The  $K_d$  values of thorium and europium for the adsorbers B, R and G are  $>10^5$ . The adsorber B shows higher adsorption also for uranium ( $> 10^5$ ), but in a narrow pH range. The adsorption of thorium and europium on the adsorbers B and R, unlike on the adsorber G, is slightly affected by calcium, magnesium, and carbonates while the uranium adsorption is affected by a carbonates concentration  $> 10^{-2}$  M. Therefore the use of the adsorber B to preconcentrate actinides, except divalent alkaline earth ions, in water analysis appears more appropriate. The adsorption pH can be kept between 8-9 to obtain the better concentration yields.

To test the use of the adsorbers B, R, and G in water analysis, 1 L of river water was filtered with a  $0.45\mu\text{m}$  porous membrane filter, the pH was kept 8 by means of Tris buffer, and  $10\mu\text{g}$  of uranium and thorium were added. 1 g of the adsorber was suspended and stirring was applied for 1 hr. The adsorbers were finally recovered by filtration and the adsorbed ions were completely eluted with 5M  $\text{HNO}_3$ . The nitric solution was submitted to I.C.P. analysis. The recovery yield was  $> 95\%$  for thorium in all cases; a recovery yield  $>95\%$  was obtained for uranium on the adsorbers B, the yield was 90% on the adsorber R, and 78% for G. In turn, considerable amounts of aluminium, magnesium and calcium were found in the solid phase, but these elements were not totally adsorbed from waters, thus indicating the greater affinity of the adsorbers toward the actinides.

Then results confirmed that the adsorbers B and R may successfully be used for the analysis of actinides, speeding up the analysis procedure.

AL and MG behave similarly. Thorium and europium are strongly adsorbed at a pH of 7-8, typical of natural waters, so the +4 and +3 actinide ions can be easily immobilised and removed from water ecosystems without preliminary pH changes. Divalent ions are also adsorbed at a pH > 8, the K<sub>d</sub> values are smaller, but high enough to allow a nearly complete absorption of the ions from basic solutions. The uranium adsorption is higher too for solutions of a pH of 7, but the formation of colloidal hydrolysed species may interfere, giving results that are not always expected.

As the capacity knowledge is important in order to employ the adsorbers for practical purposes, the cap

acity was measured by equilibrating the adsorber AL and MG with a solution of uranium or thorium 10<sup>-2</sup> M. The uranium or thorium concentration was then measured after filtration of the saturated adsorber. Differences between the initial and final concentration of the amount adsorbed was evaluated. The capacity appears directly related to phosphorous content: one mole of thorium and 0.5 moles of uranium are adsorbed per each phosphorous mole present. Therefore the adsorption mechanism of uranium and thorium appears different.

Finally the adsorbers were tested by equilibrating 1 g of adsorber with 2 L of filtered river water, to which 1-20 mg of natural uranium (as uranyl nitrate) were added. After filtration the solid phase was submitted to gamma ray analysis. The adsorption yield of <sup>234</sup>Th, in equilibrium with <sup>238</sup>U, was evaluated considering the gamma peaks at 63 Kev and 92 KeV, while the yield of uranium adsorption was evaluated by considering the gamma peak intensity at 186 KeV (<sup>235</sup>U), and comparing with a standard.

<sup>234</sup>Th is always nearly completely adsorbed as expected. Uranium adsorption yield is affected mainly from water volume used and from the adsorber amount. This behaviour is probably related to uranium hydrolysis: when uranium is added to water uncharged particles of very small size of uranyl hydroxide are formed, they and the extent of their formation cannot be quantified. Experiments carried with true polluted waters could be meaningful.

This research demonstrated that it is possible to design absorbers that are useful in a broad range of problems. In fact these absorbers, that are able to concentrate the actinides from systems of natural waters, can function in a variety of situations.

### **References**

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